Terahertz transitions in quasi-metallic carbon nanotubes

R R Hartmann[1,3] and M E Portnoi[2]

[1] Physics Department, De La Salle University, 2401 Taft Avenue, Manila, Philippines

[2] School of Physics, University of Exeter, Stocker Road, Exeter, EX4 4QL, UK

E-mail: Richard.Hartmann@dlsu.edu.ph, M.E.Portnoi@exeter.ac.uk

Abstract. We study interband dipole transitions across curvature-induced narrow gaps in quasi-metallic single-walled carbon nanotubes. The curvature effects not only open a gap in the nanotube energy spectrum but also allow optical transitions, which happen to be in the highly-desired terahertz frequency range. Applying a magnetic field along the nanotube axis allows one to tune the frequency peaks in the spectral density of absorption.

1. Introduction

Despite wide-range continuous efforts lasting for several decades [1–4], creating reliable, portable, tuneable sources and sensitive detectors of terahertz (THz) radiation remains one of the most formidable tasks of modern device physics. One of the recent trends in THz technology [2] is to use carbon nanotubes [5–6] (CNTs) as building blocks of high-frequency devices. There is a growing number of proposals using CNTs for THz applications including several schemes [7–13] put forward by the authors of the present work.

In what follows, it shall be shown that the same intrinsic curvature of quasi-metallic CNTs which opens the gap in the nanotube energy spectrum also allows strong optical transitions in the THz range. We show that the frequency peaks in the spectral density of absorption can be tuned by the application of a magnetic field directed along the nanotube axis. To illustrate that intrinsic curvature allows strong THz transitions, we shall study a subclass of these tubes, known as zigzag quasi-metallic CNTs (see Refs. [5–6] for classification of CNTs). However, the approach used herein can be generalized to all quasi-metallic tubes, all of which are expected to be optically active, since it is the curvature-induced gap, which gives rise to the strong THz transitions.

2. The band structure of quasi-metallic single walled nanotubes with curvature

Rolling a graphene sheet to form a CNT decreases the bond length to the nearest neighbors and rotates the $2p_z$orbitals, this results in the re-hybridization of the $\pi$and σ orbitals. All of the aforementioned effects result in the modification of the hopping parameters of the tight-binding Hamiltonian. In what follows we shall consider the dominant effect, that of bond length contraction. A full calculation taking into account re-hybridization shall be a subject of future study. Let us begin with the electron energy spectrum of graphene:

$$\xi(k) = s\left|\sum_{i=1}^{3} t_i \exp(i\mathbf{k}\cdot\mathbf{u}_i)\right|, \quad (1)$$

[3] To whom any correspondence should be addressed.

where $s = +1$ for the conduction band and $s = -1$for the valence band, and $\mathbf{u}_i$are the nearest neighbors vectors, which for a graphene sheet are

$$\mathbf{u}_1 = \left(\frac{a}{\sqrt{3}}, 0\right),\ \mathbf{u}_2 = \left(-\frac{a}{2\sqrt{3}}, -\frac{a}{2}\right),\ \mathbf{u}_3 = \left(-\frac{a}{2\sqrt{3}}, \frac{a}{2}\right). \quad (2)$$

Here $a = \sqrt{3}a_{CC}$, where $a_{CC}$is the nearest neighbor distance between two carbon atoms which is given as 1.42 Å. $t_i$are the tight-binding matrix elements associated with the i^{th}nearest neighbor, which for graphene are equivalent i.e., $t_i = t \approx -3$ eV. For convenience, we shall construct our zigzag CNTs such that motion is quantized alongk_y, i.e. consider $(n, -n)$ CNTs, where n must be a multiple of three. The electron energy spectrum for a quasi-metallic zigzag CNT is obtained from Eq. (1) by applying the periodic boundary condition: $k_y = 2\pi l/|\mathbf{C_h}|$, where $|\mathbf{C_h}|$is the magnitude of the chiral vector and for a quasi-metallic zigzag CNT, in the absence of curvature is given by the expression $|\mathbf{C_h}| = an$. l is an integer, which for the lowest (highest) conduction (valence) sub band is given by $l = \pm\frac{2n}{3}$. Hence, the electron energy spectrum for the lowest conduction sub band and the highest valence sub band of a quasi-metallic zigzag CNT is given by:

$$\xi(k_x) = 2s\left|t\sin\left(\frac{\sqrt{3}}{4}k_x a\right)\right|. \quad (3)$$

In the THz regime, Eq. (3) becomes $\xi(k_x) = s\hbar v_F|k_x|$, where $v_F = \sqrt{3}|t|/(2\hbar)$ is the Fermi velocity of graphene. Let us now consider the role of curvature. In rolling a graphene sheet

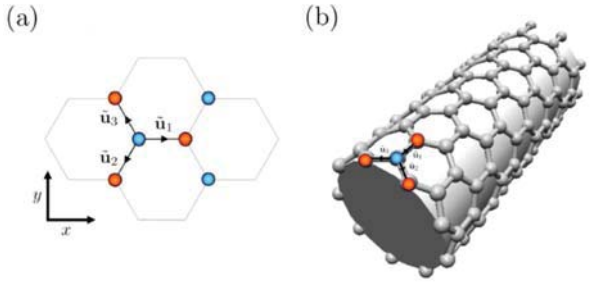

Figure 1. (a) The quasi-metallic zigzag CNT as an unrolled graphene sheet, represented by the set of effective nearest neighbor vectors$\tilde{\mathbf{u}}_i, i = 1,2,3$. (b) The quasi-metallic zigzag CNT.

to form a CNT one decreases the length of the nearest neighbor vectors. This is because the new distance is given by the chord between the two sites. One can see from Fig. 1 that upon rolling a quasi-metallic zigzag CNT, $|\mathbf{u_1}|$remains unchanged whereas the magnitude of $\mathbf{u}_2$and $\mathbf{u}_3$are reduced in comparison to that of a planar graphene sheet and their new lengths aregiven by$\sqrt{a_y^2 + \left(\frac{a}{2\sqrt{3}}\right)^2}$, where $a_y = 2R\left|\sin\left(\frac{a}{4R}\right)\right|$and R is the radius of the CNT given by$R = an/2\pi$. To understand the effects of including curvature, one can imagine the CNT as an unrolled graphene sheet, which is described by the same coordinate system as the non-curved case, but differs by a modified set of nearest neighbor vectors, $\tilde{\mathbf{u}}_i$, defined as:

$$\tilde{\mathbf{u}}_1 = \left(\frac{a}{\sqrt{3}}, 0\right),\ \tilde{\mathbf{u}}_2 = \left(-\frac{a}{2\sqrt{3}}, -a_y\right),\ \tilde{\mathbf{u}}_3 = \left(-\frac{a}{2\sqrt{3}}, a_y\right). \quad (4)$$

Therefore, the size of the chiral vector is reduced to $|\mathbf{C_h}| = 2a_y n$hence the quantization condition becomes: $k_y = \pi l/(a_y n)$.The band gap of quasi-metallic CNTs can be controlled by an applied magnetic field[14]. In the nearest-neighbor tight binding approximation the influence of a magnetic field is accounted for by adding the number $f = \Phi/\Phi_0 = eBna_y\sqrt{R^2 - a_y^2}/h$(here Φ is the magnetic flux through the polygons cross section rather than the original circular cross-section and $\Phi_0 = h/e$is the magnetic flux quantum) to the angular momentum quantum number l [6].

The effect of curvature is to break the symmetry between the nearest neighbor vectors, therefore breaking the former equivalency of t_1, $t_2$and t_3. By symmetry, the hopping parameter $t_1$does not change i.e. $t_1 = t$. The probability of hopping between sites is inversely proportional to the distance squared between hoping sites i.e. $t_i \propto \frac{1}{|\mathbf{u}_i|^2}$[15]. Hence, $t_2$and $t_3$is modified inthe same way. The modified matrix elements of hopping, $\tilde{t}_i$, are related to the original elements,t_i, by the simple relation:

$$\frac{\tilde{t}_i}{t_i} = \left(\frac{|\mathbf{u}_i|}{|\tilde{\mathbf{u}}_i|}\right)^2. \tag{5}$$

In the presence of curvature and applied field the modified electron energy spectrum for a quasi-metallic zigzag CNT is given by:

$$\xi = s|t|\sqrt{\left(\frac{\xi_g}{2t}\right)^2 + 4\lambda\sin^2\left(\frac{\sqrt{3}}{4}k_x a\right)}, \tag{6}$$

where $\lambda = -2\frac{\tilde{t}_i}{t_i}\cos\left(\frac{\pi}{n}f \pm \frac{2\pi}{3}\right)$and $\xi_g = 2|(1-\lambda)t|$. With the inclusion of curvature the spectrum is no longer linear near the crossing point (see Fig. 2) and a band gap of $\xi_g$hasappeared, whose size can be tuned by the strength of the applied field. For large radius tubesthe band gap is given by $\xi_g \approx \hbar v_{\mathrm{F}} a_{\mathrm{CC}}\left|\frac{1}{16R^2} \pm \frac{4}{\sqrt{3}a_{\mathrm{CC}}^2}\sin\left(\frac{\pi}{n}f\right)\right|$. It should be noted that assuminga different power dependence of the transfer integral on the bond length results in the same dependence of the gap size with radius [16,17] however the magnitude of the gap varies by a geometric factor. In the absence of an applied field the energy spectrum is degenerate in *l*, this degeneracy is broken for any size magnetic field hence an applied magnetic field results in two separate bandgaps. For a (24,0) CNT in zero field this gap corresponds to ≈ 1.6 THz and in the presence of a 5 T field the two gaps are ≈ 2.6 THz and ≈ 0.5 THz which correspond to $l = \frac{2n}{3}$and $-\frac{2n}{3}$respectively.

3. Optical selection rules

In the dipole approximation, the spectral density, I_ν, is given by [10]

$$I_\nu = \frac{8\pi e^2\nu}{3c^3}\sum_{i,f} f_e(k_i)f_h(k_f)\left|\mathbf{e}\cdot\langle\psi_f|\hat{\mathbf{v}}|\psi_i\rangle\right|^2\delta(\xi_f - \xi_i - h\nu), \tag{7}$$

where $\psi_i$and $\psi_f$are the eigenfunctions of the electrons in the initial and final states, $\xi_i$and $\xi_f$are their associated energies, and $k_i$and $k_f$are their associated wave vectors, $\hat{\mathbf{v}}$is the velocityoperator, **e**is the polarization of the excitation which we take to be propagating along the CNT axis and $\nu$is the frequency of the excitation. In the frame of the tight binding model, in thepresence of curvature and an applied field, the matrix element, $\mathbf{e}\cdot\langle\psi_f|\hat{\mathbf{v}}|\psi_i\rangle$can be written as

$$i\frac{a_{\mathrm{CC}}}{8}\omega_{if} + i\frac{2v_{\mathrm{F}}^2}{3a_{\mathrm{CC}}\omega_{if}}\left[1 - \left(\frac{\tilde{t}_2}{t}\right)^2\right] + i\frac{8v_{\mathrm{F}}^2}{3a_{\mathrm{CC}}\omega_{if}}\left[\left(\frac{\tilde{t}_2}{t}\right)^2\sin\left(\frac{\pi f}{n} \mp \frac{2\pi}{3}\right)\sin\left(\frac{\pi f}{n}\right)\right], \tag{8}$$

where $\hbar\omega_{if} = \xi_f - \xi_i$. Curvature not only opens the gap in the quasi-metallic zigzag CNT spectrum, but also allows dipole optical transitions at *kx* = 0 between the highest valence sub band and the lowest conduction sub band. In this regime the result should hold true across the entire class of quasi-metallic CNTs, differing only by geometrical factors. In Fig. 3 we show how the matrix element of the dipole optical transitions polarized along the CNT axis are modified in the presence of a magnetic field.

The spectral density of a zigzag quasi-metallic CNT taking into account curvature effects and applied field is obtained by substituting Eq. (8) into Eq. (7) then performing the necessary summation. In the THz regime one obtains the expression:

$$I_\nu = Lf_e(k_i)f_h(k_f)\frac{\pi^3 e^2 a_{\mathrm{CC}}^2}{3c^3h^4v_{\mathrm{F}}}\frac{\left[12t^2(1-\lambda^2)+h^2\nu^2\right]^2}{\sqrt{\lambda\left(h^2\nu^2-\xi_g^2\right)}}. \tag{9}$$

In the absence of the field, the electronic (hole) energy spectrum near the bottom (top) is no longer linear due to curvature effects and the van-Hove singularity in the reduced density of states leads to a very sharp absorption maximum near the band edge and correspondingly to a very high sensitivity of

the photocurrent to photon frequency, see Fig. 4. In the presence of an applied field, there are two absorption maxima corresponding to $l = \frac{2n}{3}$ and $-\frac{2n}{3}$ (see Fig. 5).

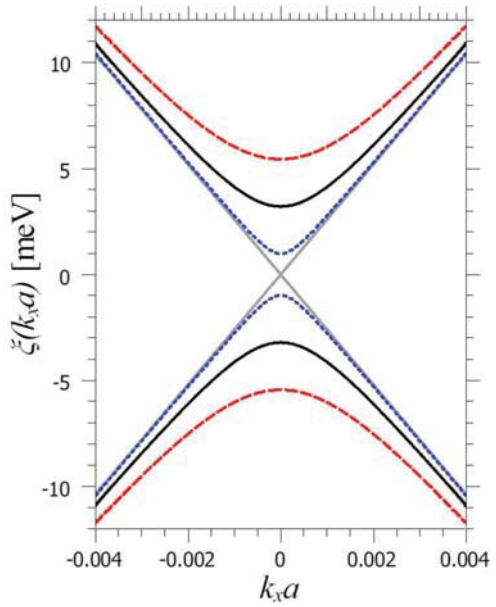

Figure 2. Detailed view of the gap for a (24, 0) CNT with (red and blue lines, corresponding to $l = \frac{2n}{3}$ and $-\frac{2n}{3}$ respectively, for the case of B = 5 T) and without (black line) an external magnetic field along the CNT axis. The grey line corresponds to zero field and no curvature.

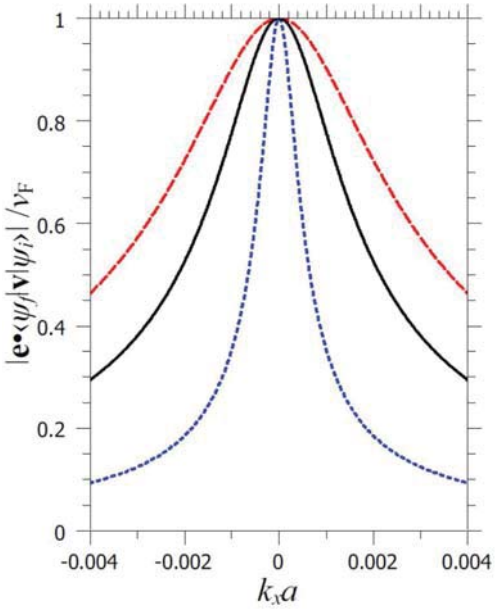

Figure 3. Dependence of the dipole matrix element for the transition between the top valence and lowest conduction sub bands on the1D wave vector k_x, for B = 0 T (black line) and B = 5 T (red and blue lines, corresponding to $l = \frac{2n}{3}$ and $-\frac{2n}{3}$ respectively) applied along the CNT axis.

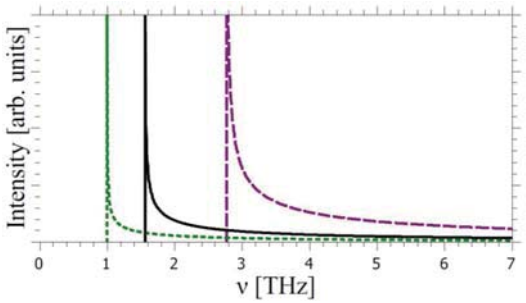

Figure 4. The calculated photon absorption spectra for a quasi-metallic zigzag CNT defined
by: (30, 0) (green short-dashed line), (24,0) (black line) and (18,0) (purple long-dashed line)

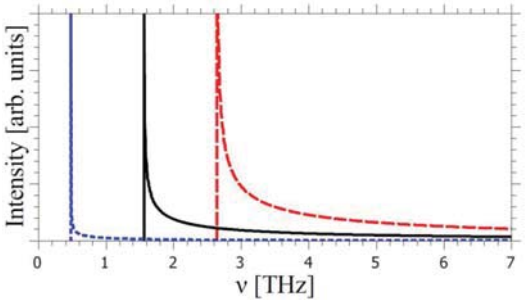

Figure 5. The calculated photon absorption spectra for a (24,0) CNT in zero field (black line) and a field of B = 5 T (red long-dashed and blue short-dashed lines, which correspond to $l = \frac{2n}{3}$ and $-\frac{2n}{3}$ respectively).

4. Conclusion

In the absence of curvature, at $k_x = 0$, optical transitions between the top valence sub band and the bottom conduction sub band in quasi-metallic CNTs are strictly forbidden by symmetry within the simple zone-folding model of the π-electron graphene spectrum. However, for zigzag quasi-metallic CNTs, dipole optical transitions are indeed allowed due to the gap opened in their energy spectrum by intrinsic curvature, which is of the order of THz. We propose that arrays of quasi-metallic CNTs could be used as the building blocks of THz radiation detectors, which would have a high sensitivity in the photocurrent to photon frequency. Furthermore, the band gap of quasi-metallic CNTs can also be controlled by an applied magnetic field, therefore allowing such devices to be tunable. Finally, our recent analysis [18] shows that the many-body (excitonic) effects, which dominate the optical properties of semiconducting CNTs [19], are also important in narrow-gap CNTs. However, due to the quasi-relativistic character of the free-particle dispersion near the band edge of the narrow-gap CNTs, there is a spectacular decrease in the exciton binding energy. Therefore, these effects do not alter significantly the main results of this paper.

5.0 References

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